Chamber Studies of Secondary Organic Aerosol (SOA) Formation

John H. Seinfeld

DOE ASP Meeting February 25-27, 2008

Conundrums

- Radiocarbon (¹⁴C) data consistently indicate that well over half of ambient SOA is of modern (biogenic) origin.
- Field measurements show correlation between WSOC (or AMS OOA spectra) and anthropogenic tracers, such as CO, suggesting that much of ambient SOA is of anthropogenic origin.
- Comparisons between ambient measured SOA and that predicted based on known precursors suggest that there is a substantial amount of "missing carbon" not in current models [De Gouw et al., 2005; Volkamer et al., 2006].

Secondary Organic Aerosol: Predictions versus Observations

Possible reasons for discrepancy between predictions and observations:

- 1. Ambient SOA yields for those parent hydrocarbons known to produce SOA exceed those measured in laboratory chambers.
- 2. Classes of SOA-forming organics exist that have yet to be studied in the laboratory or included in atmospheric models.
- 3. Uncertainties in current treatments of SOA formation in global models lead to biases that result in underpredictions.

1. Ambient SOA yields for those parent hydrocarbons known to produce SOA exceed those measured in laboratory chambers.

- SOA yields determined in laboratory chambers until recently were not fully controlled for NO_x level.
- For isoprene, monoterpenes, and aromatics, SOA yields increase strongly as NO_x decreases toward non-urban levels.
- For sesquiterpenes, SOA yields increase as NO_x increases, owing to formation of nitrate-containing products and/or efficient isomerization of alkoxy radicals to form relatively nonvolatile products (Ng et al., 2007).*

^{*} Ng, N. L. et al., Effect of NO_x level on secondary organic aerosol (SOA) formation from the photooxidation of terpenes, *ACP*, 2007.

- 2. Classes of SOA forming organics exist that have yet to be studied in the laboratory or included in atmospheric models.
 - At present, biogenic VOCs, isoprene and the terpenes, are considered as the dominant global sources of SOA.
 - Aromatic SOA production has been re-evaluated (Ng et al., 2007)* and contribution can be appreciable at the urban/regional scale.
 - Robinson et al. (*Science*, 2007): The gas-phase component of primary semivolatile OA emissions can be photooxidized to lead to SOA. This source of SOA is potentially significant.
 - Potential of both larger, e.g. diesel hydrocarbons, and smaller molecules, e.g. acetylene, to serve as parent VOCs?

^{*}Ng, N. L. et al., Secondary organic aerosol formation from *m*-xylene, toluene, and benzene, *ACP*, **7**, 3909-3922 (2007)

3. Uncertainties in current treatments of SOA formation in global models lead to biases that result in underpredictions.

- Updating of SOA yields to account for NO_x dependence, aerosol acidity, RH (Henze et al., 2007)*
- Addition of VOCs not currently considered as SOA sources, e.g. primary semivolatile VOCs
- Effect of SOA volatility (P_L° , ΔH_v) uncertain: ΔH_v estimates in current models range from 156 kJ/mol to 42 kJ/mol

^{*}Henze, D. K. et al., Global modeling of secondary organic aerosol from aromatic hydrocarbons: High- vs. low-yield pathways, *ACP*, in press.

Goals of Caltech Project

- To continue to elucidate the mechanisms of formation and SOA yields of all important classes of atmospheric hydrocarbons (to attempt to understand discrepancy between observed and modeled ambient SOA levels).
- To develop a "next-generation" SOA model, constrained by laboratory data, for inclusion in global chemical transport and general circulation models. Model should account for:

Effects of NO_x level on mechanisms

Evolution of volatility of oxidation products

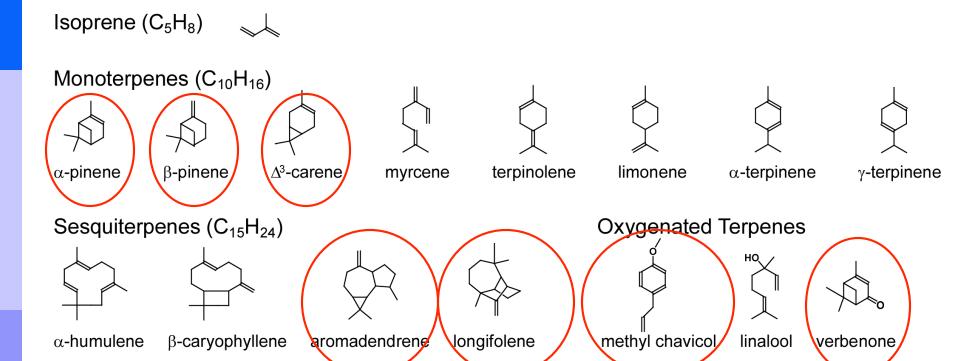
Particle-phase chemistry

Table 5. Global SOA budgets.

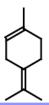
Hydrocarbon	Emission (Tg/yr)	SOA Production (Tg/yr)	Burden (Tg)
terpenes	121	8.2	0.21
alcohols	38.3	1.5	0.03
sesquiterpenes	14.8	2.0	0.03
isoprene	461	13.2	0.43
aromatics	18.8	3.5	0.08
total	654	28.4	0.78

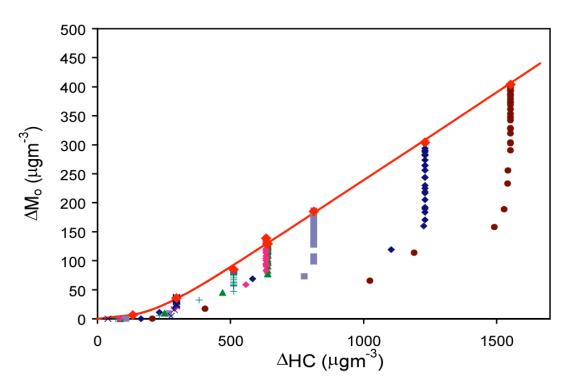
Henze, D.K. et al., Global modeling of secondary organic aerosol formation from aromatic hydrocarbons: high vs. low yield pathways, *Atmos. Chem. Phys.*, **in press.**

Biogenics



Time dependent growth vs. Final SOA growth terpinolene ozonolysis



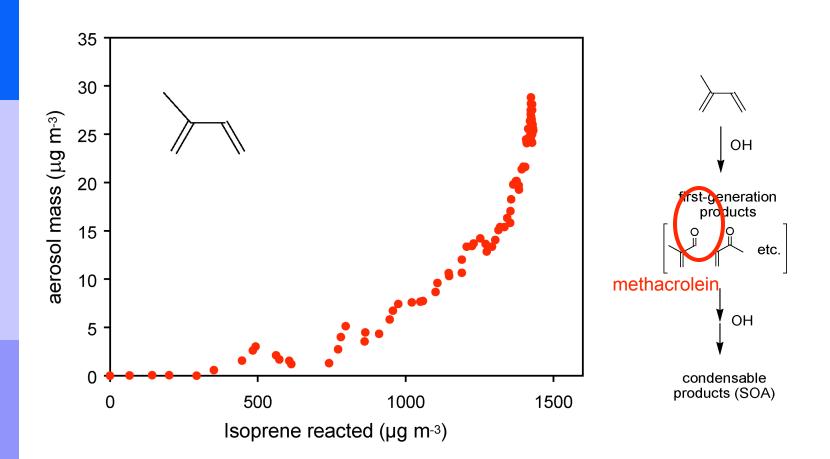


- Time-dependent growth curves and final growth curve do not overlap; timedependent growth curves show clearly the contribution of the secondary reactions
- Cannot fit the time-dependent growth curves for terpinolene ozonolysis with Odum equation, confirming that this model is only valid when the data represent final SOA growth

Isoprene (C₅H₈)

- Global emission of ~500 Tg/year [Guenther et al., 2006]
- Photooxidation of isoprene leads to SOA formation, with higher yields observed under low-NO_x conditions (~3%) [Kroll et al., 2005; Kroll et al., 2006].
- Nighttime isoprene chemistry
 - About 0.3 ppb to 2 or 3 ppb isoprene in the early evenings [Curren et al., 1998; Starn et al., 1998; Steinbacher et al., 2005]
 - Fast reaction with nitrate radicals (NO₃): 7 x 10⁻¹³ cm³ molecule⁻¹ s⁻¹ [Berndt and Böge, 1997; Suh et al., 2001]
 - Isoprene + NO₃: Source of SOA?

Isoprene and SOA formation



Global predictions of SOA from isoprene + NO₃

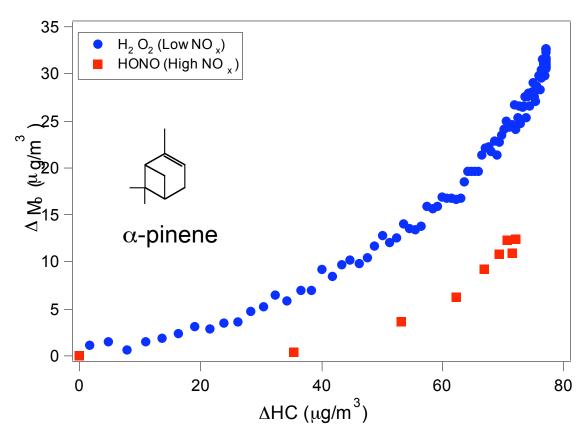
- Two global isoprene emissions are available in GEOS-Chem:
 - GEIA (Global Emission Inventory Activity) [Guenther et al., 1995]
 - MEGAN (Model of Emissions and Gases from Nature) [Guenther et al., 2006]

	GEIA	MEGAN
Isoprene emission (Tg/y)	507	389
Isoprene reacted (Tg/y) by		
Isoprene + OH	407	304
Isoprene + O ₃	69	62
Isoprene + NO ₃	29	21

Assume 10% SOA yield

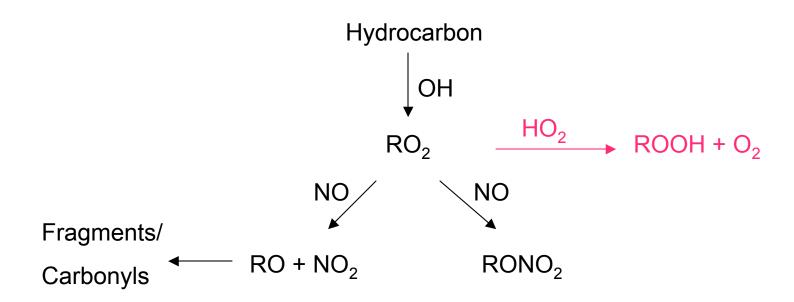
2 - 3 Tg/y SOA formed

Growth curve: α -pinene



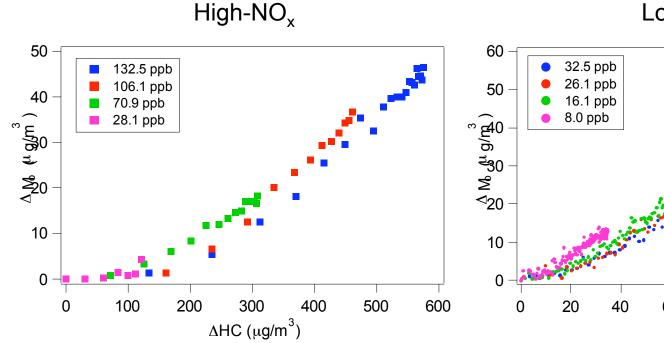
- SOA formed from the condensation of first-generation products and the first oxidation step is the rate-limiting step (*Ng et al.*, 2006)
- Same NO_x dependence as isoprene: higher NO_x , lower SOA growth

Peroxy radical chemistry

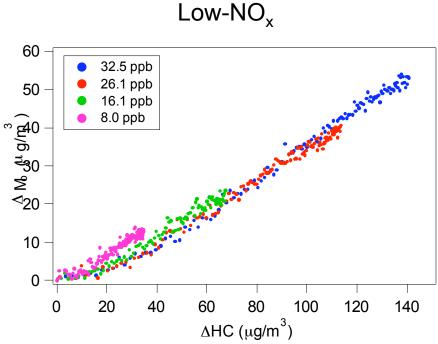


- Small alkoxy radical easily fragmented
- Organic nitrates relatively volatile [Presto et al., 2005]
- Peroxides: important SOA components [Bonn et al., 2004; Docherty et al., 2005]

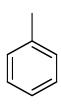
Growth curves: m-xylene



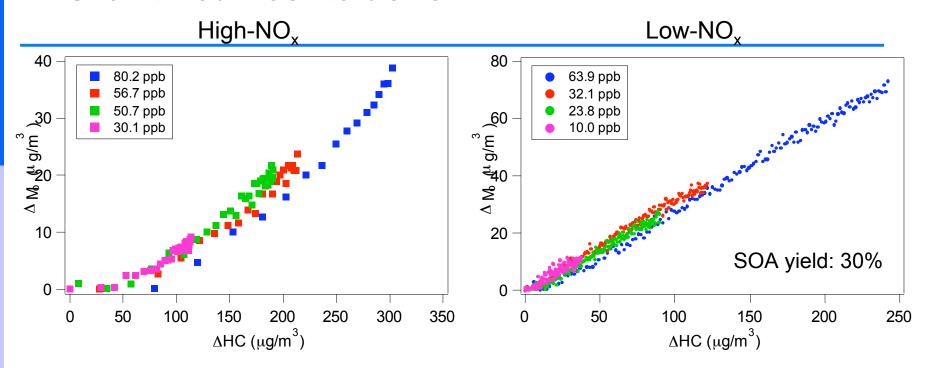
- High-NO_x: Growth curves do not overlap,
 multiple rate-limiting steps in SOA formation
 (first step is the slowest)
 S
 exp
 C
- Further-generation oxidation products



- SOA yields much higher than high-NO_x experiments
- Constant SOA yield implies essentially nonvolatile oxidation products (36% yield)

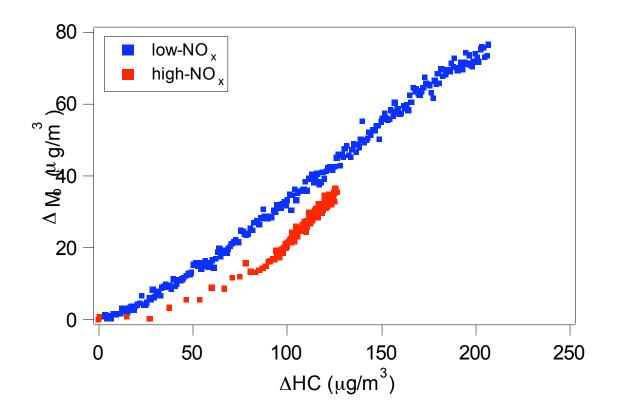


Growth curves: toluene





Growth curves: benzene



- ~400 ppb benzene (slow reaction rate, <20% reacted)
- Same NO_x dependence as m-xylene and toluene: high NO_x , lower yields
- Low NO_x: constant yield of 37%

Caltech laboratory chambers



- 2 Teflon chambers, 28 m³ each
- Scanning differential mobility analyzer (DMA): particle size distribution, volume
- Aerodyne Aerosol Mass Spectrometer (ToF-AMS): particle mass, composition
- Particle into Liquid Sampler (PILS): aerosol-phase concentrations of inorganic ions
- GC-FID: hydrocarbons
- Chemical Ionization Mass Spectrometer (CIMS): gas-phase composition
- Filter samples: off-line chemical analysis
- O₃, NO_x, RH, T
- DASH-SP: hygroscopicity

Partitioning of Products from the O3 Oxidation of a-Pinene between the Particulate and Gas Phase (Assuming a Total Organic Aerosol Mass of 50 $\mu g/m^3$)

